

## ***Interactive comment on “Aged organic aerosol in the Eastern Mediterranean: the Finokalia aerosol measurement experiment-2008” by L. Hildebrandt et al.***

### **Anonymous Referee #1**

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This paper describes AMS measurements obtained from the Finokalia site on Crete in the eastern Mediterranean Sea during the EUCAARI intensive during May 2008. The paper focuses on the age of the organic aerosol and demonstrates that all the organic material arriving at the site was highly aged. Unlike other locations no primary aerosol could be discerned. Factorisation methods were employed on the OA mass spectra to identify if different OA was present and a thermal denuder was used to identify if this was related to volatility. This was found not be the case and the paper demonstrates that when highly aged the volatility of the aerosol is relatively invariant. Furthermore there was little evidence of chemical variability in the OA from the different sources. In all this paper present a very useful insight into aged organic continental aerosol

C436

for comparison with many more numerous near field studies. It is very well written and used an appropriate number of clearly readable and well annotated diagrams. I recommend this paper for publication in ACP. I have some comments that the authors could use to further add to the paper. Most importantly, I think that the authors have an opportunity for extending the discussion of the representation of ageing as presented in recent papers by Ng et al and Morgan et al and also to discuss the volatility of OA in the far-field compared to that in the near-field (e.g. Huffman et al, Lanz et al and Grieshop et al). This rounded discussion may set a broader context.

Page 1849 line 9: it should be explicit that you are referring to fine mode inorganic material

Page 1850 line 4: “Ageing and,” should read “Ageing, and”

Page 1850 line 12: It should be stressed that these classification are typical. Certain environments may produce other factors though these are not common.

Page 1850 : It seems strange that after quoting Ng et al 2009 earlier the authors don't reference it at this point as it, and the partner paper Morgan et al 2009, describe the dynamic ageing of OA in a consistent framework.

Page 1851 lines 12-17: Given the premise of the paper it would be good to state what criteria were used by Koulari et al 2008 for identifying the sources of aerosol.

Page 1852 line 22: It may be worth a brief synopsis of the detailed published work on the prevailing meteorology simply to provide a context for the field study presented in this paper.

Page 1853 line 6: “. . .is presented in companion publications” should be “. . .are presented in companion publications”

Page 1853 line 12: Given no active drying was installed, it may be worth commenting on the relative temperatures in and outside the laboratory.

C437

Page 1853 line 19: was the nephelometer sampling dry aerosol or were these deliquesced for some or all of the time?

Page 1854 line 9: This is written generally, was the AMS used in this project operated with a high throughput lens?

Page 1855 line 26: The oxygenated ion at  $m/z$  57 should be  $C_3H_5O^+$

Page 1857: Sections 2.3.3 to 2.3.5 are too short to form full sections, it would be better if they were merged.

Page 1858: lines 18-19 e.g. should be i.e. and it is stated that  $y$  is the mean value for the whole campaign. This should be given an overbar.

Page 1858: line 20: "C is the amplitude, k is the harmonic number," should be "C<sub>k</sub> is the amplitude of the kth harmonic, . . ."

Page 1860 lines 9-19: The CE of the AMS: The CE is derived from the comparison between the volume derived from the SMPS weighted by the component densities and the AMS mass distribution. Figure 2 shows that the peak in the mass distribution of the AMS is shifted to large sizes, presumably because the aerosol is well aged. However, this means that much of the AMS mass may well be above the size of the majority of channels of the SMPS. What was the largest size of the SMPS scan? And what were the uncertainties in the comparison based on counting statistics from the SMPS? If not all the volume was captured by the SMPS then the derived CE will be biased high and may be closer to 0.5. Whilst the aerosol is slightly acidified, it does not appear to be greatly so from the data shown in figure 1. What was the calculated humidity in the line based on in and outside T and outside humidity? Figure 3 shows good agreement between measurements of sulfate and OM from the AMS, steam-jet and filters. This is good evidence that the CE was correctly estimated but no comment is made in this section.

Page 1860 line 25: repetition of site

C438

Page 1861 line 23: It is peculiar to cite a personal communication with a co-author.

Page 1861 lines 21-23: One wonders whether the differences in the size distributions between sulfate and OM is due to change in the sulfate:OM over time. The sulfate mass is much higher than the OM in periods of long range polluted transport compared to other periods but the OM does not change too much. It is not inconceivable that the size distribution of sulfate and possibly also OM increased during long range pollution transport. If a campaign average is taken then the average size will be shifted in proportion to the mass.

Page 1862 line 11: How well has the zero calibration of the nephelometer been applied? It may be possible that this is a real offset in that instrument.

Page 1863: The discussion of the rather weak dependence on subsequent photochemical processing time of OA that has aged by more than one day already is a useful one. I would have liked to have seen this developed so that the result is compared with previous experiments (e.g. Volkamer et al; Morgan et al) and results from chamber studies.

Page 1865 lines 20-28: The discussion at this point may give the reader the impression that the chemical processes acting on this aerosol are different from those observed to be acting elsewhere. The key difference is one of age of the aerosol. As I am sure the authors are well aware the biggest reason for the inverse correlation between f44 and volatility in other lab and near pollution field studies is that there is substantial change in chemistry of the ensemble OA due to oxidation and f44 reflects the balance between the more and less processed organic material. Whereas in their study the ageing process is much further advanced and there is little fresh material to affect the f44 throughout the experiment. I think that this discussion could be better developed.

Page 1866 lines 20-22: In the nomenclature of the introduction any OPOA is indistinguishable from added SOA. This probably should be stated.

C439

Page 1866 lines 24-25: Is  $R=0.07$  really significant? I suggest not.

Page 1866-1868: This discussion is a very useful one and more the clearer and readable for the details of the PMF being separated to the appendix. Elsewhere in the paper the authors quote Ng et al 2009, this paper, and Morgan et al 2009, seek to demonstrate the continuum nature of the transition of OOA as a function of age in the atmosphere. What the authors of this paper add to the Ng et al and Morgan et al descriptions of organic aerosol is evidence that volatility changes appear minimal in aged aerosol. It would be worth discussing the ageing of OOA as seen by Ng et al and Morgan et al and to link this to the previous measurements of volatility closer to source (Huffman et al) and in laboratory studies (Grieshop et al) at this point. Like this paper, Morgan et al show little evidence for HOA in their flights across Europe.

Page 1869 lines 1 to 8: This is very long winded. The mass spectra of the two factors show  $m/z$  43 is higher in B than A and hence there is bound to be a correlation between  $f_{43}$  and OOAB and  $f_{44}$  and OOAA. The needs to be stated concisely and that is all.

Page 1869 line 13-17: The lack of variation in OA despite seeing changes in diurnal oxidation also implies that the pool of gaseous precursor for SOA formation is small as the photochemical oxidation rate is high, driven by OH.

Page 1870 line 9-17: If the total amount of OM (gas and particulate) varies with major pollution source but the ageing process has removed all of the gas phase precursor pool before reaching the site then conceivably OOAA may vary with source simply because there was more precursor. This also has the potential to explain the observations.

Page 1871 lines 9-11: Again, it would be very useful for the ageing processes discussed by Ng et al and Morgan et al 2009 to be included here. The authors highlight very similar phenomena and present a situation that is at the far field limit of the ageing cycle, providing a very useful end point in the processing of OM. I realise that both of these papers were submitted close to concurrently with this paper, however the au-

C440

thors o cite one of the papers and a rounded discussion here would be a very robust conclusion to the paper.

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C441